



TITLE:

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CITATION:

Urayama, Kenji ...[et al]. Swelling Behavior of Polybutadiene Networks in Nematic Liquid Crystal Solvents (STATES AND STRUCTURES-Polymer Condensed States) .. ICR Annual Report 2000, 6: 8-9

ISSUE DATE:

2000-03

URL:

<http://hdl.handle.net/2433/65246>

RIGHT:

Swelling Behavior of Polybutadiene Networks in Nematic Liquid Crystal Solvents

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Degree of equilibrium swelling (Q) of polybutadiene networks in four nematic liquid crystals (LCs) has been investigated as a function of temperature by cross-polarized microscopy. Phase behavior of the LCs in the networks has also been observed. It has been found that the nematic-to-isotropic phase transition temperatures of the LCs in the networks (T_{NI}^g) are slightly (ca. 1K) lower than the ones of the corresponding pure LCs (T_{NI}^o), and that the depression degrees of T_{NI} in each system are comparable in spite of large differences in Q between every system. In the temperature regions of $T_{NI}^g < T < T_{NI}^o$ where the LC phases inside and outside gel are different, Q is almost constant against temperature change.

Keywords : Swelling/ Polymer network/ Polymer gel/ Liquid crystal/ Nematic-to-isotropic phase transition

Swelling is an interesting property specific to polymer gels together with rubber elasticity. Degree of swelling of polymer gels significantly depends on the environments such as the nature of swelling solvents, temperature etc. which influence the thermodynamic interaction between the constituent polymer and the solvent. Most of the earlier studies are focused on the swelling in conventional isotropic solvents, but few studies on the polymer gels swollen in anisotropic solvents, i.e., liquid crystal (LC) solvents are reported so far. Polymer network swollen in LC solvent is expected to exhibit some unique physical properties originating from nematic-to-isotropic phase transition and nematic character of the LC solvents. Especially, the effect of the nematic-to-isotropic phase transition of LC (as swelling solvent) on the degree of equilibrium swelling (Q) is an interesting subject. In the present study, we have critically investigated the temperature dependence of Q especially in the close vicinity of nematic-to-isotropic phase transition temperature (T_{NI}) using four chemically stable LC solvents with vary-

ing structure [1].

Cylindrical polybutadiene (PB) gels with a diameter of less than 1mm were immersed in the LC solvents in an optical cell at certain temperatures until the equilibrium swelling was achieved. Four LC solvents, 4-octyl-4-biphenyl carbonitrile (**I**), 4-(*trans*-4-pentyl-cyclohexyl) benzonitrile (**II**), 4-(cyanophenyl-4-heptyl) benzoate (**III**) and 4-4'-diheptyl azoxybenzene (**IV**) were used as swelling solvents. The phase and swelling behaviors were examined with Nikon cross-polarized microscope equipped with Mettler Hot stage FP-82 under nitrogen atmosphere. T_{NI} of LC solvent was determined as the temperature at which the nematic texture appears in the cooling process. The degree of equilibrium swelling (Q), defined as the ratio of the gel volumes in the dry (V_o) and equilibrium swollen state (V), was calculated from the diameter of the gels in the dry (d_o) and swollen state (d) under the assumption of isotropic swelling using the relationship, $Q = V/V_o = (d/d_o)^3$.

Cross-polarized microscopic observation reveals that the LC solvents outside or inside the gels have different

STATES AND STRUCTURES — Polymer Condensed States —

Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution, and in situ studies on structural formation/change in crystalline polymer solids.



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T_{NI} for all the systems studied. The LC solvent outside the gel corresponds to the pure LC solvent. T_{NI} of the LC inside and outside gel, designated as T_{NI}^g and T_{NI}^o respectively, are displayed in Table 1. T_{NI}^g of all the systems are 0.7–0.9 degree lower than T_{NI}^o . In the temperature range $T_{NI}^g < T < T_{NI}^o$, the LCs outside or inside the domain of gels form two different phases: nematic and isotropic respectively. The corresponding appearance of the surrounding solvents and gel remain bright and dark, respectively, under cross-polarized microscope. The slightly lower T_{NI}^g compared to T_{NI}^o can be qualitatively explained by taking into account of the impurity effects of the polymer backbone of the gels on the phase transition of the LCs. However, it is noteworthy that the degrees of depression in T_{NI}^g in each system are comparable (0.7 to 0.9 degree) regardless of the considerable differences in Q values (impurity content) at T_{NI}^g between every system. For example, the polymer volume fractions in the gels ($\phi=1/Q$) containing **I** and **III** at T_{NI}^g are ca. 0.14 and ca. 0.49, respectively, corresponding minimum and maximum among the four systems. In our previous communication, we reported that T_{NI}^g of the PB gels in a nematic LC (EBBA) was much higher than T_{NI} of the uncrosslinked PB solution of EBBA with the same PB content, i.e., T_{NI}^g was not so much depressed as expected from the impurity content [2]. In the present study, the independence of T_{NI}^g values on ϕ observed also implies that the depression in T_{NI}^g can not be simply explained in terms of only the impurity effect. Interaction between LC solvents outside and inside gel leading to promote the nematic phase formation inside gel, if present, may explain the unexpected non-sensitivity of T_{NI}^g to ϕ for the present systems. The study for this problem is now in progress.

Temperature (T) dependence of the degree of equilibrium swelling (Q) for the PB gel in LC **I** is shown in figure 1. In general, Q tends to increase with increase in temperature. The magnitude of Q in the isotropic phase is larger than that in the nematic phase. The following features for the T dependence of Q around T_{NI} are commonly observed for all the systems as evidenced by the inset of the figure: (i) The Q - T curves show plateau regions at around T_{NI} with no appreciable change in Q ; (ii) A finite abrupt (discontinuous-like) change in Q values is observed at certain temperatures around T_{NI} .

In the temperature range of $T_{NI}^g < T < T_{NI}^o$ which is characterized by a plateau region for Q , the LC solvents inside the gel are isotropic, whereas the solvents outside are in their nematic phase. It appears that such a phase difference prevents the flow of LC solvents between outside and inside the gels and the swelling practically stops showing almost constant value of Q against the temperature change. The discontinuous-like change in Q is observed at certain temperatures for all the systems. But the degree of discontinuity is much smaller than that observed in some gels showing typical volume phase transition. Without application of any external fields, LC in the nematic phase has poly-domain nematic structure where

the anisotropic nature of nematic LC is macroscopically cancelled out. The slight discontinuity of volume change should be attributed to the screening effect of poly-domain nematic structure on the anisotropic characters of nematic LC molecules. However, the effect of the formation of the poly-domain nematic structure on the thermodynamic interaction between the PB and LC is still large enough to cause an appreciable, though small, discontinuous-like change in gel volume. Formation of mono-domain nematic structure, under the application of external field, where the LC molecules are macroscopically aligned in a unique direction is expected to induce significant change in thermodynamical interaction leading to large discontinuous volume change. Swelling in a mono-domain nematic LC solvent using external electric field is our future subject to study.

References

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2. Urayama K, Luo Z, Kawamura T and Kohjiya S, *Chem. Phys. Lett.*, **287**, 342 (1998).

Table 1. Nematic-to-isotropic phase transition temperatures of liquid crystalline solvents outside (T_{NI}^o) and inside (T_{NI}^g) poly(butadiene) gel, and polymer volume fraction (ϕ) in the gels at T_{NI}^g .

LC	T_{NI}^o /K	T_{NI}^g /K	ΔT_{NI} /K	ϕ at T_{NI}^g
I	313.6	312.9	0.7	0.26
II	327.3	326.4	0.9	0.14
III	328.1	327.4	0.7	0.49
IV	343.5	342.6	0.9	0.32

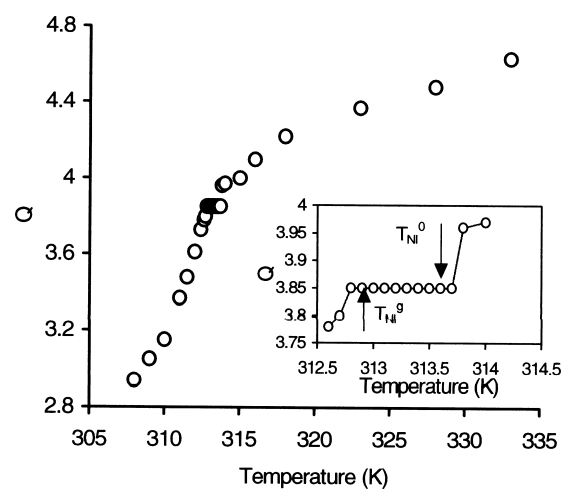


Figure 1. Temperature dependence of degree of equilibrium swelling (Q) of PB gel in LC **I**. The inset is for the vicinity of T_{NI} .